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Modelling of phase distributions in MCrAlY coatings and their interactions with nickel based alloys

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Abstract. At high operating temperatures the oxidation resistant MCrAlY (M=Ni, Co) coatings and the substrate alloys are highly susceptible to phase changes, particularly, after long hours of exposure. With the advent of computational modelling involving metallurgical thermodynamics and diffusion parameters in recent times, it is now possible to follow these phase changes and interdiffusion processes through simulation. In the present work, phase changes in the temperature range between 950 and 1050 ^{0}C in the MCrAlY coating materials containing additions of Cobalt and Rhenium have been determined through such an approach. Further, using a diffusion simulation software interdiffusion between a commercial NiCoCrAlY coating and a Nickel-base superalloy substrate material at 1000 ^{0}C has been simulated. The simulated results have been compared with the experimental findings and they are found to be in reasonable agreement with each other. Some deviations observed are discussed in the light of limited availability of thermodynamic and kinetic data.

1. INTRODUCTION

In recent years gas turbine manufacturers are demanding higher operating temperatures for achieving improved efficiency [1]. At these high temperatures the oxidation resistant MCrAlY (M=Ni, Co) coatings and the substrate alloys interact which could result in phase changes. This can be expected especially at the interfaces as well as in the sub-scale depletion layer beneath the alumina based surface scale. Even minor modifications in the composition of the base alloy or in the composition of the MCrAlY coating can substantially affect the phase equilibria and the interdiffusion properties [2, 3]. Computational modelling of these processes in addition to experimental determinations would thus be of great advantage for the estimation of long-term component performance and for the selection of optimum coating/substrate combinations. A major requirement for the modelling of interdiffusion processes is a reliable description of the phase equilibria in the MCrAlY coating.

Phase diagram calculations for Ni-based superalloys by the CALPHAD and other methods have been extensively carried out by Saunders and others [4, 5]. The results of these calculations have shown high quality predictions for various aspects of phase equilibria in the multi-component system Ni-Al-Co-Cr-Hf-Mo-Nb-Ta-Ti-W-Zr-B-C [4]. The author observed a high degree of agreement between the calculated γ, γ' and liquid phase equilibria and the experimental measurements.

The objectives of the present study have been to evaluate how accurately the phase equilibria in a newer type of MCrAlY coating system can be modelled and to assess, computational modelling of

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interdiffusion between the MCrAlY coating and a Ni-based superalloy substrate with a commercially available software and database.

2. MODELLING BACKGROUND

In the present work a commercially available Thermo-Calc [6] software package has been used for the computational determination of phase equilibria. The main approach of these programmes is a Gibbs free energy minimisation process performing multicomponent calculations. All the relevant thermodynamic coefficients and kinetic factors, which uniquely describe the properties of the various phases, are held in the databases of the software. A more extensive description of the modelling procedures can be found in reference [7]. Substitutional type and multiple sub lattice models are the main models used to describe phase formations. Ni-DATA [8] has been used as database in the current simulation work and this is a modified version of the database used by Saunders [4], incorporating data additionally for elements Fe, Re and N. The same database has also been used in the subsequent modelling of interdiffusion between a commercial NiCoCrAlY coating and Nickel-base superalloy substrate material using the DICTRA software [9]. For these simulations a model for diffusion in dispersed systems integrated in the DICTRA software has been used. In this model diffusion is assumed to take place in the matrix phase only. The dispersed phase/s present acts/act as point sink or sources of solute in the simulation and its fraction and composition are calculated from the average composition in each node under the assumption of local equilibrium. A detailed description of simulation methodology can be found in References [10, 11]. The diffusion couple was formed between 2 mm of the substrate alloy and 0.3 mm of the bond coat thickness. The simulations were done at an exposure temperature of 1000 ^{0}C up to 3000 h. They were performed initially with time steps of 108000 seconds and with a labyrinth factor of 1+3*(1-volfr)/volfr ("volfr" means the fraction of the volume of precipitate particles to the total volume of the matrix phase [9]) and subsequently refined with time steps of 1080 seconds.

3. MATERIALS SELECTED FOR MODELLING

The nominal compositions of the cast model alloys for experimental studies are shown in Table 1. All alloys on which high temperature phase stability studies have been carried out contained 0.4%Y in accordance with most commercial coatings. However, Y is not taken into account in the modelling, as it is not included in the Ni-DATA base used in the present work. It is assumed, that this does not lead to substantial errors due to the very low Y concentration.

Table 1. Nominal composition of the Model MCrAlY alloys.

Model Alloy	Composition in Mass %				
	Ni	Co	Cr	Al	Re
FKA	Bal	0	20	3	0
FKB	Bal	0	20	6	0
FKC	Bal.	0	20	9	0
FKD	Bal.	0	20	12	0
FLW	Bal.	20	20	3	0
FLA	Bal	20	20	6	0
FLB	Bal.	20	20	9	0
FLC	Bal.	20	20	12	0
RE19	Bal.	20	20	9	1
RE20	Bal.	20	20	9	3
RE21	Bal.	20	20	9	5

The interdiffusion simulation studies were performed on a typical commercial turbine blade material, CMSX 4, as the substrate alloy and PWA 286 as the MCrAlY coating material. The chemical compositions of these alloys are given below:

Alloy	Ni	Co	Cr	Al	Ti	Ta	Mo	W	Re	Hf
CMSX-4 Substrate	Bal	9.0	6.5	5.6	1.0	6.5	0.6	6.0	3.0	0.1
PWA 286 Bond coat	Bal	22.0	17.0	12.5	-	-	-	-	-	0.25

4. EXPERIMENTAL WORK

An extensive experimental programme [12] has been carried out involving the alloys listed in Table 1. The thermal stability studies included heating the alloys to specific temperatures of 950, 1000 and 1050 ^{0}C in an argon atmosphere for 100 h and subsequently water quenching to freeze the high temperature microstructure. Optical microscopy, SEM and EDX have been used for the characterisation of the microstructures with respect to their constituents and phase compositions. Experimental results are presented only as representative examples in the case of each set of alloys studied and for comparison with the calculated values. In the case of diffusional studies the diffusion couple of the substrate alloy and the bond coat was exposed to 1000 ^{0}C for 1000 h in an argon atmosphere.

5. MODELLING, EXPERIMENTAL OBSERVATIONS AND DISCUSSION

5.1 Phase Change Studies in Co-free and Co-bearing MCrAlY Coating Alloys

Using the Thermocalc software package, the phase fractions have been calculated in the Co-free ternary Ni-20Cr-xAl and in the Co bearing quaternary Ni-20Cr-20Co-xAl coating alloys at aluminium levels from 3 to 12 % (Table.1). The phases have been calculated in the temperature range between 950 to1050 ^{0}C and the changes in the phase constituents and contents (npm = number of moles of a phase) are graphically presented in the Figure 1.

Addition of 3% Al in the Co-free or in the Co-bearing alloys did not alter the γ-phase structure of the alloys in the range of temperatures simulated and, hence, has not been shown in the graphical presentations. Examining the simulated results for Ni-20Cr-xAl alloys it is seen that at an Al content of 6% there are no phase changes between 950 and 1050 ^{0}C, it remains $\gamma + \gamma'$ at all temperatures. However, the relative amounts of these phases change drastically. The γ' content decreases from about 30-vol % at 950 ^{0}C to practically zero at 1050 ^{0}C. A large phase change is observed with the addition of 9% Al to the alloy system, in which, there is an exponential increase of γ' phase to nearly 90 vol % at 950 ^{0}C. Small amounts of α phase also start forming at this composition. This simulated prediction is in tune with the earlier observations made with regard to Al additions to high Cr-content Ni-based coating alloys [13]. The $\gamma + \gamma' + \alpha$ phase field changes to $\gamma + \gamma' + \beta$ on heating to 1000 ^{0}C, which on subsequent exposures to 1025 and 1050 ^{0}C shifts from $\gamma + \gamma' + \beta$ to $\gamma + \beta$ respectively. Further increase of the Al content to 12 % causes β phase formation in place of γ even at 950 ^{0}C, whereas γ' remains stable at about 50-vol %, a small amount (~10 vol %) of α phase is also being present.

Considering the phase changes in the Co-bearing Ni-20Cr-20Co-xAl coating alloys, it is observed that the addition of Co has resulted in the formation of β phase in place of γ' at 950 ^{0}C, practically at all Al levels. At 6% Al there are no phase changes at simulated higher temperatures except for a small increase in γ phase content with the corresponding decrease in β content. Further increasing the Al content to 9% has resulted in higher amounts of β phase formation at the cost of γ phase and these two phases remain very stable at all elevated temperatures. A small amount of σ-phase has been predicted in the alloy when the Al content is increased to 12 %. The following phase changes have been determined in the case of a Ni-20Cr-20Co-12Al alloy if the temperature is changed from 950 to 1050 ^{0}C: $\gamma + \beta + \sigma \rightarrow \gamma + \beta \rightarrow \gamma + \beta \rightarrow \gamma + \beta$. This indicates the σ phase dissolution temperature to be around 1000^{0}C, which is in reasonable agreement with the predictions of

Saunders [4] for some Nimonic type alloys Thus, the modelling indicates the optimum Al level to stabilise a two phase $\gamma + \beta$ structure without σ in the Ni-Cr-Co-Al coating alloys, in the range of Cr and Co contents studied, to be approximately 9%.

The related experimental results evaluated by microstructural features with respect to three investigated temperatures are presented for a Co-free and a Co-bearing coating alloy containing 12 % Al (Figure 2).

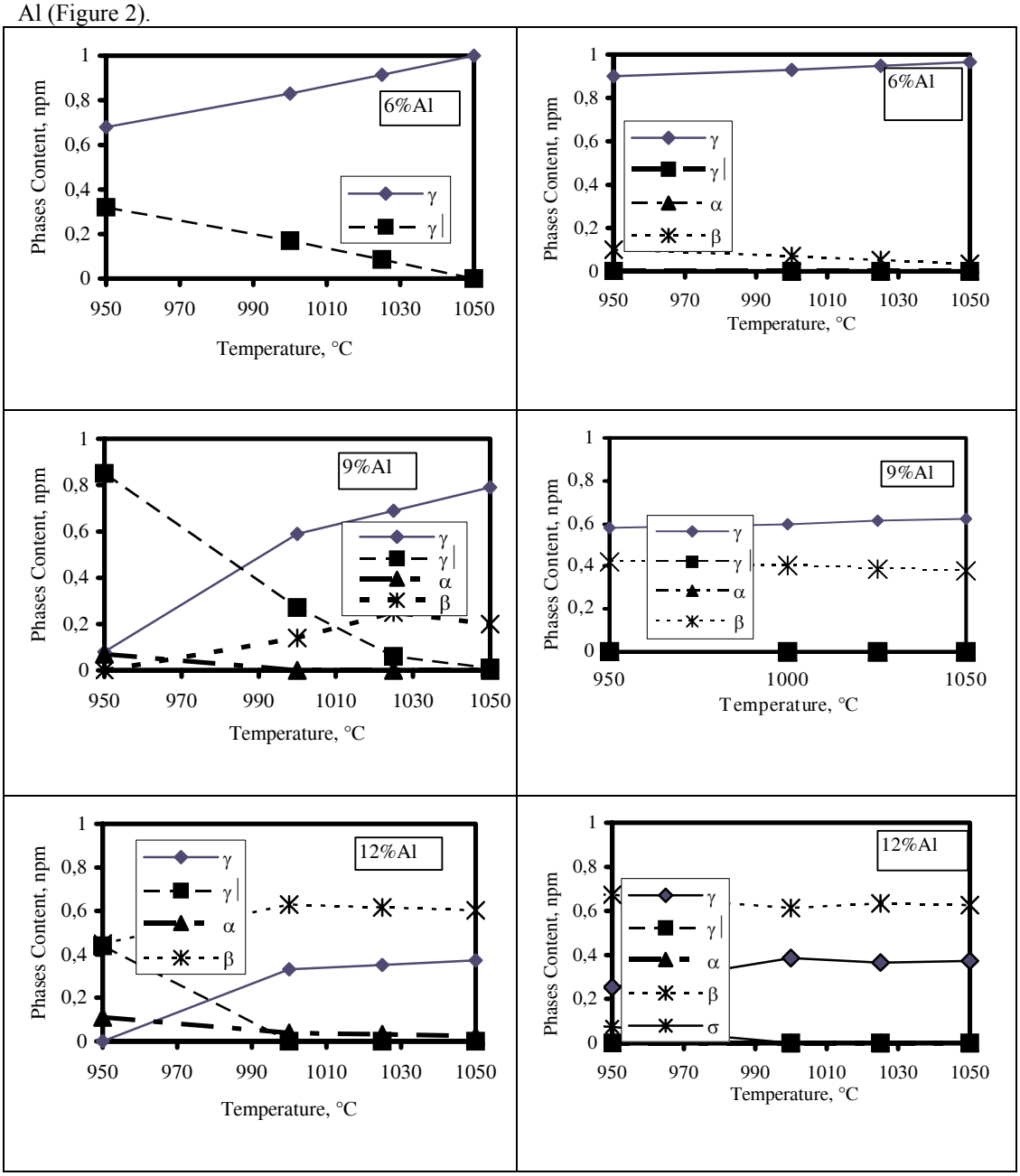

Figure 1. Simulated phase changes in the Co-free Ni-20Cr-xAl (left column) and in the Co-bearing Ni-20Cr-20Co-xAl (right column) coating alloys as function of temperature.

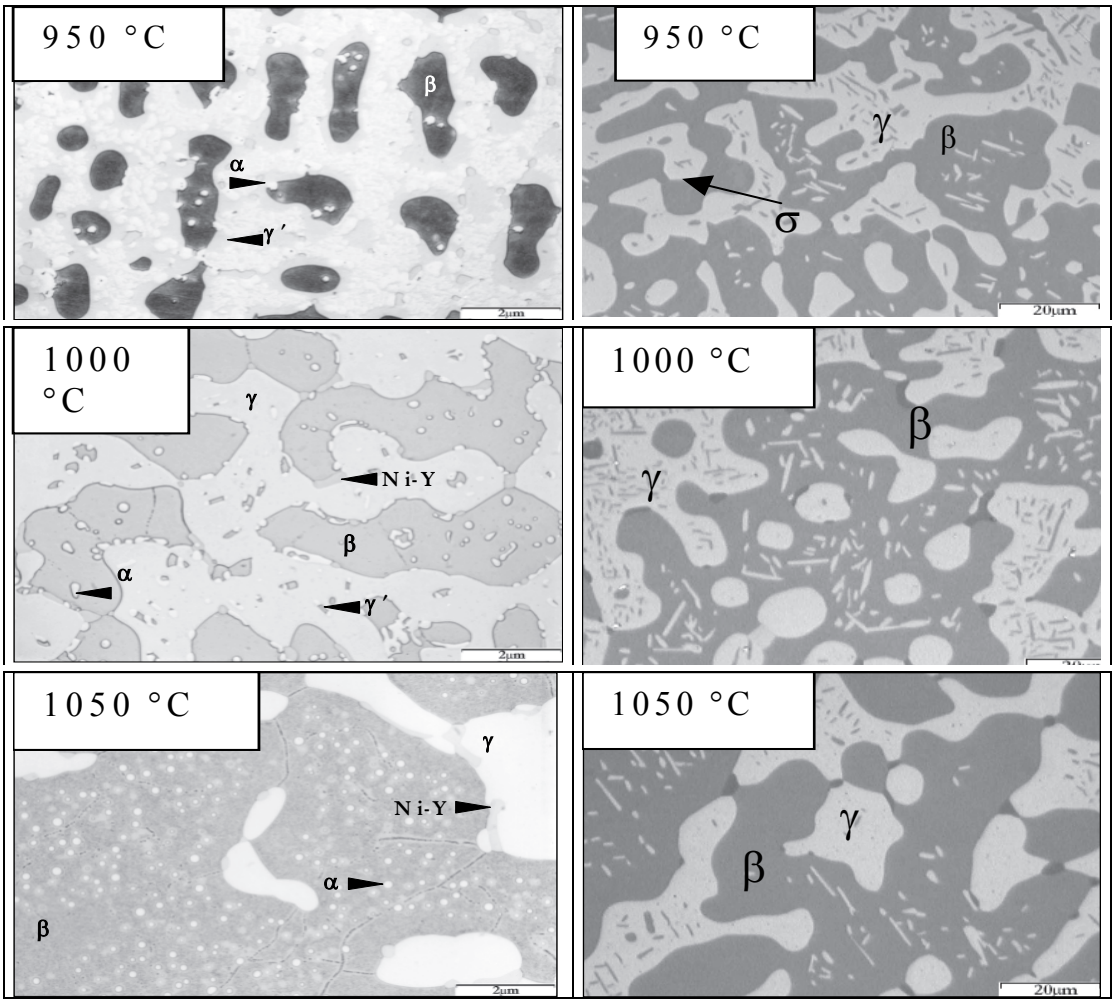

Figure 2. Microstructural changes in the Co-free ternary Ni-20Cr-12Al (left column) and Co-bearing quaternary Ni-20Cr-20Co-12Al (right column) coating alloy at different temperatures.

Following the sequential microstructural changes for the Co-free alloy in Figure 2 it is observed that at 950 ^{0}C it consists of γ', β and α, whereby the large grains of β-phase are surrounded by the γ' phase. This phase exists also as needle-like precipitates within the β phase grains. Large amounts of α phase are observed and the NiY intermetallic is also identified. At 1000 ^{0}C the microstructure consists of γ instead of γ' as large grains whereas, the other phases observed at 950 ^{0}C remain stable at this temperature. Small amounts of γ' phase regions have also been noticed within γ region. A large number of α (Cr)–precipitates are present within the β phase. Finely distributed NiY precipitates are also detected. A similar microstructure is observed at 1050 ^{0}C but without any γ'. Thus, the experimentally determined phase changes on exposure to 950, 1000 and 1050 ^{0}C are $\gamma' + \beta + \alpha \rightarrow \gamma + \beta + \gamma' + \alpha \rightarrow \gamma + \beta$, respectively. At 1000 ^{0}C the experimental microstructure shows a four phase field of $\gamma + \gamma' + \beta + \alpha$, which can only exist as an invariant point in the ternary system, while, the model has correctly predicted only a three phase field of $\gamma + \beta + \alpha$. This alloy lies close to the phase boundary between the $(\gamma' + \alpha)$ and the $(\gamma' + \beta + \alpha)$ phase fields in the ternary phase diagram Ni-Cr-Al. It is obvious that, when the alloy composition lays on or close to a phase boundary even minor variations in compositions may lead to major fluctuations in the predicted phase equilibria.

The microstructural characteristics of the Co-bearing Ni20Cr20Co alloy with 12% Al at 950 ^{0}C reveals γ, β and σ (Co, Cr)- phases, again in combination with finely distributed NiY precipitates. At 1000 ^{0}C the structure consists mainly of large γ and β-phase grains. Within these grains of γ and β there are fine precipitates of β and γ, respectively. The σ phase did not exist at this temperature and, hence, its dissolution must have occurred in the temperature range between 950 and 1000 ^{0}C, agreeing well with the modelled prediction. The microstructure at 1050 ^{0}C is primarily the same as at 1000 ^{0}C with the difference that there are no needle-like precipitates within the large grains of γ and β- phases. These experimental results thus confirm that the σ (Co, Cr)-phase is stable in MCrAlY- systems with high Cr and Co contents. Thus, the experimentally determined sequential phase changes from 950 ^{0}C $\rightarrow$ 1000 ^{0}C $\rightarrow$ 1050 ^{0}C are the same as found by modelling i.e. $\gamma + \beta + \sigma \rightarrow \gamma + \beta \rightarrow \gamma + \beta$.

5.2. Phase Change Studies with Re in Co-bearing Alloys

The results of the phase simulations in the case of Re additions into the Ni-20Cr-20Co-9Al alloys are presented in Figure 3. Addition of Re results in an increasing amount of σ phase from 0 to about 10 volume % with a corresponding decrease in γ. phase content. However, the β phase formed remains stable at all temperatures studied. In other words, addition of Re effectively suppresses the dissolution of β phase, which explains the experimental observations made in actual coating systems, that addition of Re reduces the width of the β-depleted zone beneath the alumina surface scale [14]. The modelling predicts relatively stable

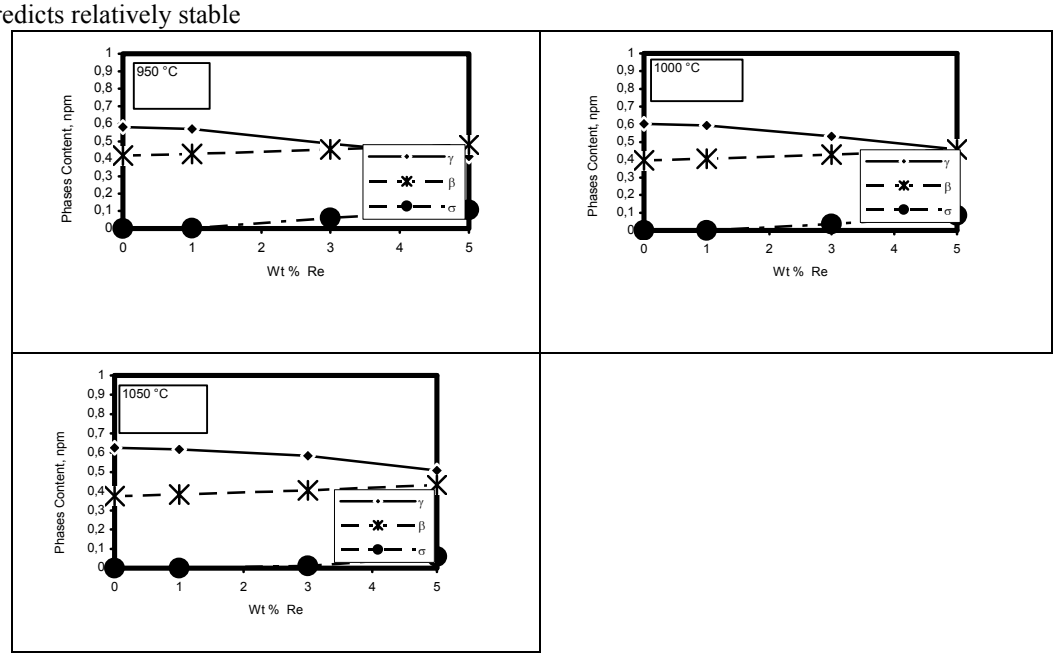

Figure 3. Effect of Re content on phase equilibria in quaternary Ni-20Cr-20Co-9Al coating alloys at different temperatures.

phase constituents for these coating alloys in the temperatures range between 950 and 1050 ^{0}C, viz. γ +β from 0 to1% Re and $\gamma + \beta + \sigma$ for alloys containing above 1 %. The simulated predictions are compared with the experimental microstructural results in Figure 4.

The microstructural features of these alloys were produced after a homogenisation treatment at 1100^{0}C in an argon atmosphere. The Re free Ni-20Cr-20Co-9Al coating alloy has been predicted to consist of γ and β phases only at 1050 ^{0}C. This is in agreement with the experimental results, except for the NiY precipitates.

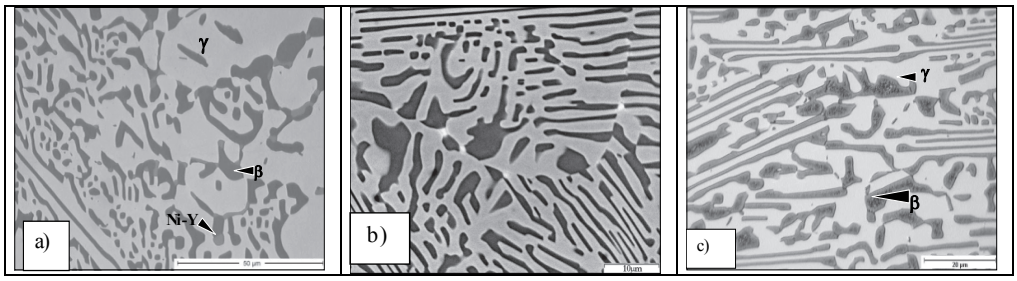

Figure 4. Effect of Re content on microstructural changes in the quaternary Ni-20Cr-20Co-9Al coating alloy – a) 0% Re-optical microscopic picture, b) 3% Re-SEM image, c) 3% Re-optical microscopic picture.

5.3 Diffusion Studies

Initially all the elements present in the CMSX 4 and the PWA 286 coating alloy were entered in the input data for diffusion simulation but this led to integration failures and simulations could not be completed. Subsequently, only the major constituents of the alloys, viz. Ni, Cr, Co, Al and Ti were entered, as suggested in the software for such situations and simulations completed. Thus, the following effective compositions in wt % have been entered in the simulations: CMSX 4; Cr = 6.5, Co = 9.0, Al = 5.7 and Ti = 7.5, Ni = Rest: PWA 286; Cr = 17.4, Co = 22.0 Al = 13.35 Ni=Rest. In these calculations, the elements with similar effects on phase stabilities are taken together, thus the amounts of Cr is taken as Cr + Si, Al as Al + Hf or Al +Hf + Y, Ti as Ti + Ta and reminder of the alloying elements are added to Ni, in the appropriate situations. The initial phase constituents with these compositions for the two alloys calculated by THERMOCALC yielded 17% γ + 83 % γ′ for the substrate alloy and 30% γ + 70% β for the coating alloy. The γ-phase was assumed to be the matrix phase in all simulations, while the γ′– and β–phases were the so-called dispersed phases. The results of these interdiffusion simulations corresponding to 1000 h have been compared with respect to the phase and composition changes across the interface with the experimental results obtained after 1000 h exposure at 1000 ^{0}C (Figure5).

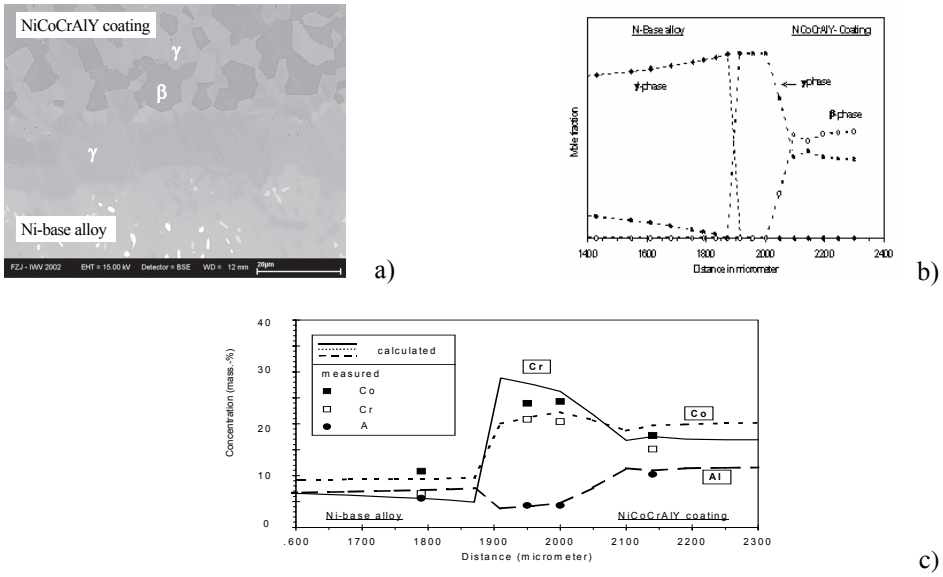

Figure 5. Interface between Ni-Base Alloy (CMSX 4) and NiCoCrAlY (PWA 286) coating after 1000 h exposure at 1000°C. a) SEM-picture, b) calculated phases c) measured and calculated element concentrations.

The interdiffusion width across the interface was calculated to be about 100μm, however, smaller diffusion width was observed in the microstructure. The γ′-phase in the substrate destabilised on diffusion of Co from the coating and has resulted in the formation of high amount of γ-phase in its place. The β-phase at the interface also gets dissolved due to loss of Al. In other words, the phase movement from the substrate to the bond coat across the interface can be described as $\gamma + \gamma' \rightarrow \gamma \rightarrow \gamma + \beta$. These movements completely agree with the experimental results in Figure 5a and also with earlier published work [9]. There is also reasonable good agreement between simulated and measured element profiles.

6. CONCLUSIONS

The modelling is able to predict the phase equilibria in typical commercial ternary NiCrAl coating alloys with reasonable accuracy. Largest deviations between calculations and experimental results were observed for a high-Al coating alloys at temperatures around 1000 ^{0}C, because even slight temperature changes lead to large fundamental changes of the phase equilibria at this temperature. Cobalt additions to the system primarily stabilise γ and β phases. This is practically so at all temperature and Al addition levels, thereby suppressing γ′ formation and at high Al contents, σ phase is initiated. The addition of Re can lead to very substantial changes in the relative amounts of phases present in the system. It promotes formation of σ phase in the system even at low concentrations. However, the σ phase so formed becomes less and less stable at higher exposure temperatures. Long term high temperature exposure effects on substrate and bond coat materials in the MCrAlY coated Ni-base alloy can be effectively studied through simulation modelling with a reasonable degree of accuracy.

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